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Light modulation in phase change disordered metamaterial - A smart cermet concept

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A B S T R A C T

Cermet coatings are popular solar selective absorbers as they allow capturing most of the solar energy while minimising radiative losses. Embedded metallic nanoparticles in dielectric matrices promote multiple internal reflection of light and provide an overall low emissivity. VO₂ in the metamaterial state is regarded in this study as a responsive mixed phase comprising metallic rutile VO₂ inclusions in semiconducting monoclinic VO₂ phase mimicking cermet. The smart cermet responds to thermal stimuli by modulating the size of the metallic inclusions and thereby enabling the manipulation of their interaction with light. The highly reliable and reproducible response of the smart cermet corroborates with the observed ramp reversal memory effect in VO₂. We demonstrate a thermally controlled 85% emissivity switch taking advantage of the narrow hysteresis and tuning abilities of the disordered metamaterial.

Keywords:

Metamaterial
Smart cermet
Vanadium oxide
MOCVD
Emissivity control
Solar selective coatings
Semiconductor-metal transition

Introduction

Cermets are metal-dielectric composites in which metal particles are embedded in dielectric matrices as displayed in Fig. 1. Cermet coatings are used as effective spectrally-selective absorbers due to their high solar absorbance and low thermal emittance [1,2]. The properties of the cermet strongly depend on the volume fraction of the metal inclusions in addition to their chemical nature, size, shape and dispersion within the matrix [3]. Nevertheless, the properties of the cermet coatings are frozen upon synthesis as the parameters influencing the optical properties can no longer be altered. Therefore, the development of traditional cermet materials for light modulation sounds compromised.

One of the most popular and well-studied mechanisms for light modulation relies on materials with engineered structures to influence the nature of light. These materials are known as metamaterials and the phenomenon of light modulation through engineered surface modifications is termed as optical topological transition [4,5]. Perfect solar absorbers based on metamaterials were demonstrated by fabricating specific shapes and

configurations of metallic structures on dielectric matrix. By varying the size and configuration, the spectral window of the perfect absorption can be adjusted [6,7].

Relevant research was reported on emissivity control devices for their implementation in space applications. Programmable emissivity switching is crucial for spacecraft and satellite surfaces, but their implementation often includes tedious fabrication process comprising bulky and energy inefficient mechanisms [8–11]. Significant research has been done in the field of thermal management for spacecraft and satellites, due to varying exposure to sun illumination. Variable heat rejection surfaces are used to control the heat dissipation mechanisms. One of the earliest techniques of thermal management of spacecraft is by the use of mechanical or electric louvers, where actuating the louvers exposes or conceals a section of surface with a contrasting emissivity, thereby reflecting the IR radiation on demand. Electric louvers based on micro-electro-mechanical systems (MEMS) were introduced to further improve the same mechanism and miniaturise the package [9]. Here micro-sized windows open and close on demand to reject IR radiation. An advantage of MEMS based louvers over their bulk mechanical counterparts is the possibility to achieve partial IR rejection by actuating only a part of the micro-louvers [9]. Electrochromic devices that rely on chemical changes to vary the

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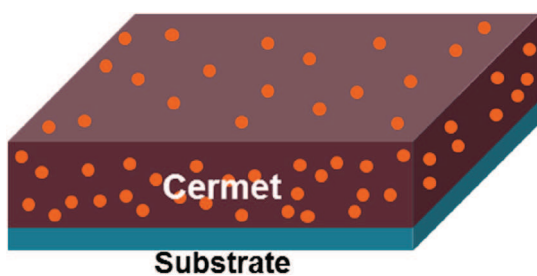


Fig. 1. Schematic presentation of cermet coating.

emissivity of the surface are investigated as alternative solutions to change the optical properties of the radiating surface. An electrically triggered redox reaction on conductive polymers leads to a change of emissivity ($\Delta\epsilon$). The absence of moving parts is advantageous in terms of production cost, reliability and integration [10]. Nevertheless, slow switching; high input power and the relatively low $\Delta\epsilon$ remain clear drawbacks. This strengthens the need of developing variable emissivity coatings that offer large amplitude of emissivity change, with negligible switching delay and low actuation power. The coatings should also virtually have no loss in performance over a longer time period and should resist environmental degradation. Therefore, inorganic metal oxide coatings with intrinsic phase transition behaviour are an appealing alternative. Ideally the phase transition occurs instantaneously between two strongly contrasting emissivity states without involving any chemical change.

An ideal candidate for such application would be a coating material that switches reliably between distinct values of emissivity, and which is simple to fabricate and integrate, while consuming fraction of the power needed for existing technologies.

Vanadium dioxide is a strongly correlated material featuring a semiconducting-to-metal transition (SMT) near room temperature. In contrast to the metallic phase, the low temperature semiconducting phase features high infrared transmission and high thermal emissivity. The transition occurs with a narrow hysteresis, revealing a temperature range (64–68 °C) where vanadium oxide features the coexistence of the metallic and semiconducting phases. This, so called disordered VO₂ metamaterial is analogous to a cermet. Upon the increase of temperature, metallic inclusions nucleate and grow throughout the semiconducting phase [12]. In this article we introduce the concept of “smart cermet” material with tuneable optical properties based on disordered VO₂ metamaterial. The concept of tunability is addressed by temperature-enabled control of the size and density of metallic particles in the dielectric matrix which in turn vary the emissivity of the coating. The unique feature of VO₂-based smart cermet is that, both dielectric matrix and metallic particles are one and the same material at different phases. Therefore, a single layer of VO₂ can be manipulated to feature (i) a fully dielectric state, (ii) a variable state with metallic inclusions embedded in the dielectric matrix, or (iii) a fully metallic state, by controlling the temperature at which it is operated. Such characteristics are not accessible with conventional cermet coatings. Thermally triggered emissivity modulation is emphasized in this study.

Methods

VO₂ films were deposited on silicon substrates using direct liquid injection MOCVD (MC200 from Annealsys), which is a stagnation point-flow warm-walled reactor. Cyclohexane solution containing 5×10^{-3} mol/l of vanadium (IV) oxy-tri-isopropoxide [VO(OC₃H₇)₃] is used as a precursor feedstock that was

maintained under nitrogen atmosphere at room temperature before its injection into the evaporation chamber. The precursor delivery was performed at a frequency of 2 Hz and a feeding rate of 1 g/min. The pressure and temperature of the evaporation chamber were maintained at 0.6 mbar and 200 °C during deposition respectively. The substrate is maintained at 600 °C during the 2 h of deposition and the subsequent heat treatments.

One hour annealing was performed right after the deposition under oxygen partial pressure of 1×10^{-2} mbar. The sample is then further subjected to annealing under vacuum acting as a reducing atmosphere for 4 h. The chamber is allowed to cool down to withdraw the sample. All depositions were carried out on 4-inch silicon wafers with an upper native oxide layer. Uniform and high quality VO₂ films were observed throughout the wafers with excellent homogeneity.

Film thickness was measured using an Alpha step d-500 profilometer from KLA-Tencor, whereas the Infrared image analysis was conducted using the FLIR X6580SC thermal camera operating in the spectral range of 1.5–5.1 μ m. A CVD-grown CNT on silicon was used as a reference black body for an accurate determination of temperature, which is necessary to assess the emissivity change of coated VO₂. Precise temperature control was achieved through a Linkam TMS heating stage with programmable heating and cooling profiles. The stage is widely used for its accurate temperature control of heating/cooling rates with high ability to maintain a particular temperature for extended periods (>100 h) and has the ability to increase or decrease the temperature at the rate of up to 150 °C/min with no measurable overshoot. The heating or cooling pulses are programmed, and the set values are produced with divergences less than 0.01 °C. The inspection of the surface morphology was performed by Scanning Electron Microscopy (SEM) at a working distance of 4 mm and an acceleration voltage of 5 kV. It is worth mentioning that the electron beam of the SEM induces the SMT of VO₂ from the semiconducting monoclinic phase to the metallic rutile, which is beneficial for the charge dissipation. The identification of the crystalline phases was performed with X-ray diffraction (XRD: Bruker D8 and with CuK α as the X-ray source) and Raman scattering (InVia, Renishaw with a 532 nm laser).

Results and discussion

The process used for the synthesis of VO₂ includes CVD deposition and an oxidative sintering as a post-deposition heat treatment. Using this process the deposition rate was evaluated at ~10 nm/min. The prepared films are clearly identified as monoclinic VO₂ at room temperature by Raman spectroscopy. Displayed spectrum in Fig. 2a features all characteristic Raman bands of the VO₂ monoclinic phase, which can be clearly distinguished from the other phases of vanadium oxide [13]. The obtained films do not feature any Raman band above 68 °C, which indicates the occurrence of a structural transition.

The room temperature X-ray diffractogram, Fig. 2b, of the obtained films confirms their identification as crystalline monoclinic VO₂. The SEM surface inspection, Fig. 2c, reveals a dense structure with large grains witnessing an efficient sintering of the film.

Thermal camera was implemented in this study to investigate the VO₂ phase transition from semiconducting monoclinic to the metallic rutile that occurs with thermal cycling. As the metallic phase features a low thermal emittance, the surface appears colder above the transition upon heating, a phenomenon that was termed as negative differential thermal emittance [14]. The VO₂ emissivity versus temperature upon cycling between 60 and 70 °C, Fig. 3, features three distinct regions marked (a), (b) and (c). During heating stage the system undergoes an abrupt semiconductor to metal transition (SMT) at 67.5 °C resulting in an emissivity drop

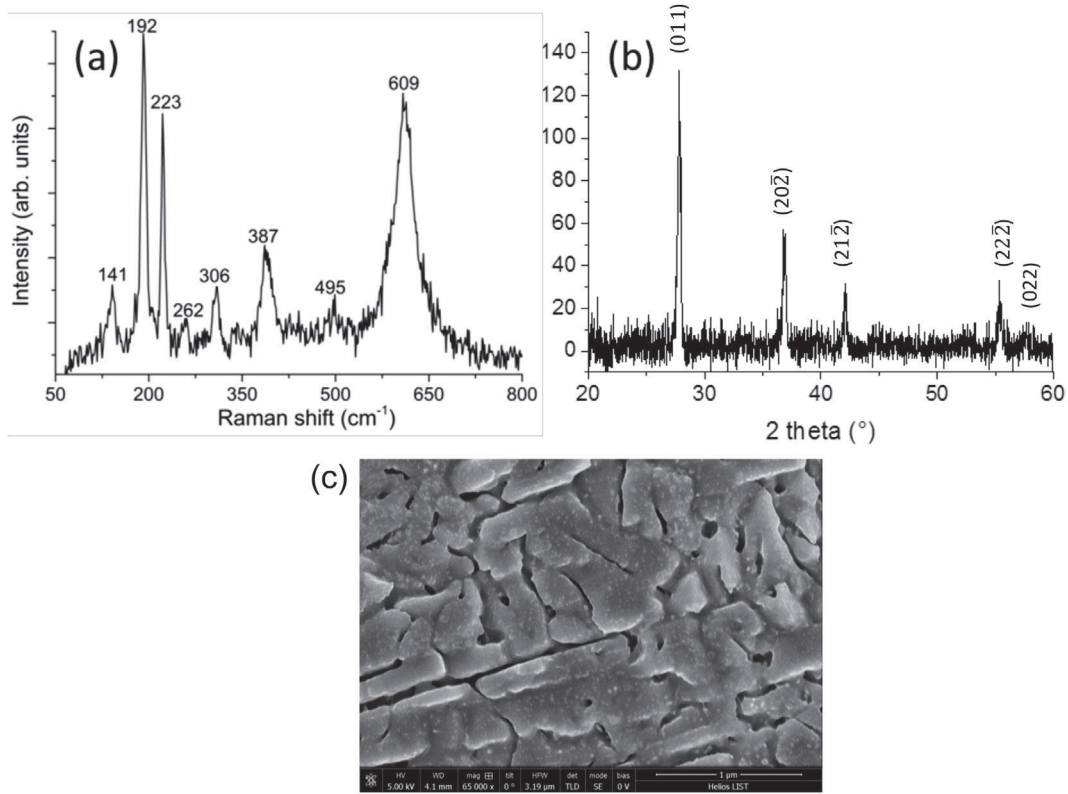


Fig. 2. Raman scattering (a), XRD (b) and the SEM (c) surface morphology of the VO₂ obtained via oxidative sintering. The (hkl) assignments correspond to the monoclinic VO₂ reference pdf no. 44-0252, featuring the P21/a symmetry.

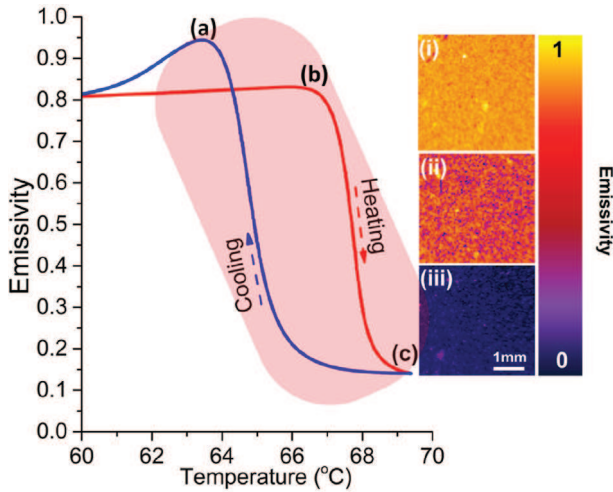


Fig. 3. Temperature-dependent emissivity of VO₂ across the SMT and the infrared images of three selected regions (a-i, b-ii and c-iii) on the hysteresis curve. Meta-material region is shown as a shaded area on the hysteresis curve.

from 0.8 to 0.1 within a ΔT of 2 °C. The infrared images in Fig. 3 (i), (ii) and (iii) provide a visual representation of the material undergoing SMT, by formation of metallic puddles in the semiconducting phase, which grow in number and coalesce, thus making the whole layer metallic. These metallic puddles reflect infra-red radiation and lower the overall emissivity [12–14].

In the cooling stage, emissivity features a transient peaking up to 0.94 at 63.5 °C marked as (a) in Fig. 3. This peculiar peak of emissivity is highly reproducible and is systematically observed for

all performed coatings. This kind of negative differential thermal emittance was previously reported by Kats et al. [14,15] where VO₂ as a tuneable phase change material was shown to operate both as perfect emitter [14] and absorber [15]. The peak in the emissivity curve is attributed to the formation upon cooling of nanoscale metallic inclusions in an arrangement that maximizes light absorption. At 63.5 °C the density and size of the metallic inclusions align in such a way that a near perfect thermal emittance is reached. The demonstrated, Fig. 3, change in emissivity from 0.8 to 0.1 ($\Delta\epsilon = 0.7$), or 0.94 to 0.1 ($\Delta\epsilon = 0.84$) using VO₂ coatings, is unprecedented with conventional variable emissivity coatings used in space applications [16,17].

Perfectly reversible and reliable emissivity transition is recorded for VO₂ films during extended thermal cycling tests. Furthermore, the transition characteristics were shown to be insensitive to the cycling rate. The stability of the metamaterial state is demonstrated in a previous work, where Raman mapping of the mixed phase region was reported over 100 h to obtain a spatial mapping of the metallic inclusions in the semiconducting matrix [13].

The metallic inclusions nucleate and grow upon heating, and shrink to disappear in the cooling stage. During a subsequent cycle, IR imaging reveals the nucleation of the metallic phase exactly at the same positions and confirms its systematic growth in an identical manner as the preceding heating cycle for consecutive cycles. This behaviour is in line with the ramp reversal memory effect in VO₂ reported recently [18], where the nucleation of the metallic puddle during the heating cycle occurs at the same spot over successive cycles. This behaviour is of paramount importance for a tuneable and reliable light modulation.

The polycrystalline nature of the films results in a random strain field distribution across the film. As the transition temperature of VO₂ is significantly influenced by the stress [19,20], crystallites do

not switch to the metallic state at the same temperature. Therefore, metamaterial state with a memory effect occurs as a result of scattered stress-induced early switching crystallites.

It is largely accepted that VO_2 undergoes a first order phase transition from a semiconducting monoclinic M1 to a metallic Rutile (R) phase. Recent studies, have however firmly established the formation of a second monoclinic phase, M2, as an intermediate between M1 and R [19,20]. Although the formation of M2 phase is not detectable by infrared imaging, spatial Raman mapping reported earlier [13], we have shown that certain regions of the film undergo the M1-M2-R transition pathway whereas other regions undergo a direct M1 to R transition. The transition temperature (T_c) as indicated in Fig. 4a when compared/superposed on to the VO_2 stress-phase diagram [20] evidences the presence of tensile stress

in the films and implies the formation of the M2 intermediate phase. It is generally possible to generate a stress map starting from the temperature-dependent thermal imaging.

Fig. 4b compares the thermal emissivity hystereses extracted from various restricted surface areas of a few μm^2 (referred to as site 1, 2 & 3). The thermal emissivity at the microscopic scale reveals significant differences in the transition temperature reaching up to 0.3 K. In contrast, measuring successive hystereses at the same restricted areas shows no measurable difference and the curves cannot be discerned from each other. This observation brings further evidence to the involvement of the stress field distribution and its relation with the robust memory effect. Despite the surface heterogeneity, the memory effect enables a perfect reversibility of thermally controlled thermal emissivity as

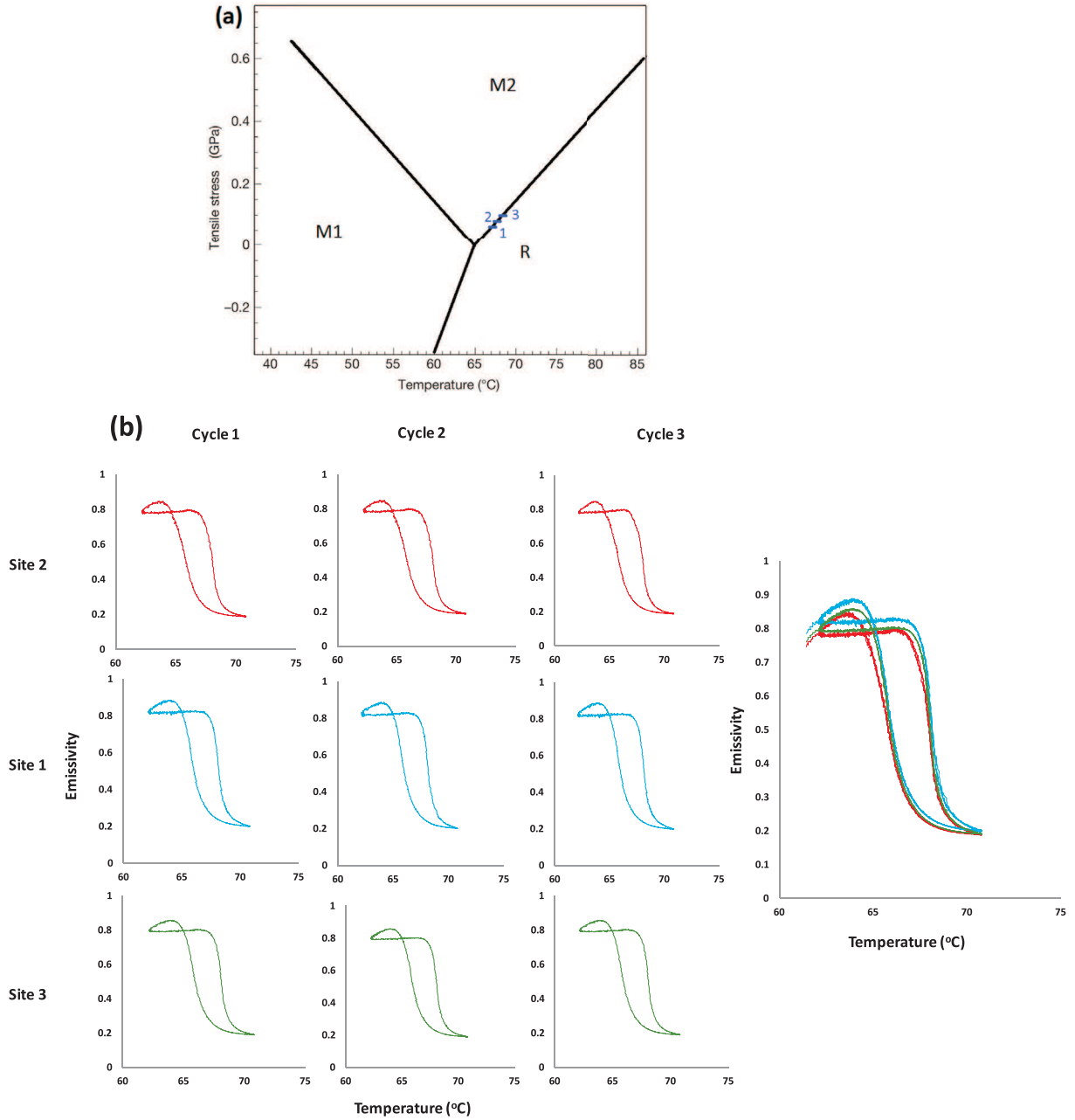


Fig. 4. (a) Transition temperature measured by an IR camera at three different restricted sites are marked over the strain-phase transition diagram [20] of VO_2 revealing the strained nature of the films. (b) Emissivity versus temperature curves for the three sites over multiple temperature cycles shows no change what so ever in between successive cycles. Whereas upon comparing ϵ vs T curves for all sites together, we notice a minor difference in the peak emissivity and the T_c .

measured at the macroscopic scale.

VO₂ metamaterial coatings offer a superior flexibility compared to traditional cermet coatings which feature fixed distribution and density of metal particles. Guo et al. [21] described how metallic inclusions can be engineered to tailor matter-light interaction. Authors reviewed the applications of metallic nanostructures for light trapping in solar energy-harvesting structures and devices from thin film photovoltaic cells to solar thermal structures [21]. Therefore, by controlling the size, shape and density of metallic inclusions, VO₂ coatings clearly place themselves as an attractive and versatile all-oxide alternative. Tuneable emissivity provides a fertile ground for the design and integration of innovative smart light modulation functionalities in existing technologies.

Fig. 5 displays emissivity tuning by adjusting the cooling and heating cycles in the metamaterial region. By limiting the extent of cooling to the temperature enabling the maximal emissivity (marked by a blue circle in Fig. 5b) and beginning the heating stage in the subsequent cycle (Fig. 5c), it is possible to take benefit of the observed emissivity spike to further enhance the amplitude of the emissivity change. The described control of temperature ramp yields tuneable emissivity of VO₂ metamaterial between 0.94 and 0.1. Fig. 5b–f highlight the possibility to adjust the emissivity between 0.1 and virtually any intermediate value, ≤ 0.94 , by appropriately selecting the minimal cooling temperature. Similar approach can be implemented to enable emissivity change between 0.94 and virtually any intermediate value, ≥ 0.1 , by appropriately selecting the maximal heating temperature. The memory effect enables in our study adjusting and maintaining the system at specific values of emissivity. Therefore, the temperature is a reliable parameter to precisely control the overall cermet architecture.

Other heating-cooling cycles can be conveniently designed to adjust both the minimal and maximal emissivity values within the 0.1–0.94 range. As the semiconductor to metal transition of VO₂ occurs in picosecond time scale [22,23], a high-speed light modulator can be designed.

Thermally controlled switching of emissivity in VO₂ films is demonstrated in Fig. 6a. Initially VO₂ films are stabilized at a steady temperature of 68 °C in the metallic state with low emissivity. A programmed transient temperature dip (cooling pulse) of $\Delta T = 1.5$ °C drives the system to switch from a low emissivity state at $\epsilon = 0.1$ to a high emissivity state at $\epsilon = 0.94$. A programmed transient temperature increase (heating pulse) of similar amplitude drives the system back to the low emissivity state. This way, VO₂ in the disordered metamaterial state can be used as an optical switch with controlled emissivity that correlates directly with the infrared reflection. Therefore, the smart cermets can be explored for applications as a shutter and IR light modulation. A contrasting triggering profile in Fig. 6b highlights the versatility of switching patterns. By maintaining the system at a steady temperature in the middle of the hysteresis loop, emissivity switching is achieved by providing tiny temperature pulses in either direction. Small energy inputs lead to large changes in emissivity, thereby making them highly efficient and low power consuming alternatives to existing emissivity control devices.

Coatings, exhibiting emissivity control and infrared modulation require micro fabrication and additional processing challenges like multilayer deposition, MEMS fabrication and patterning [8,11,24–26], all of which increase the complexity and cost of the end product. Due to the intrinsic property of VO₂ coatings, no additional processing or patterning steps are required to achieve

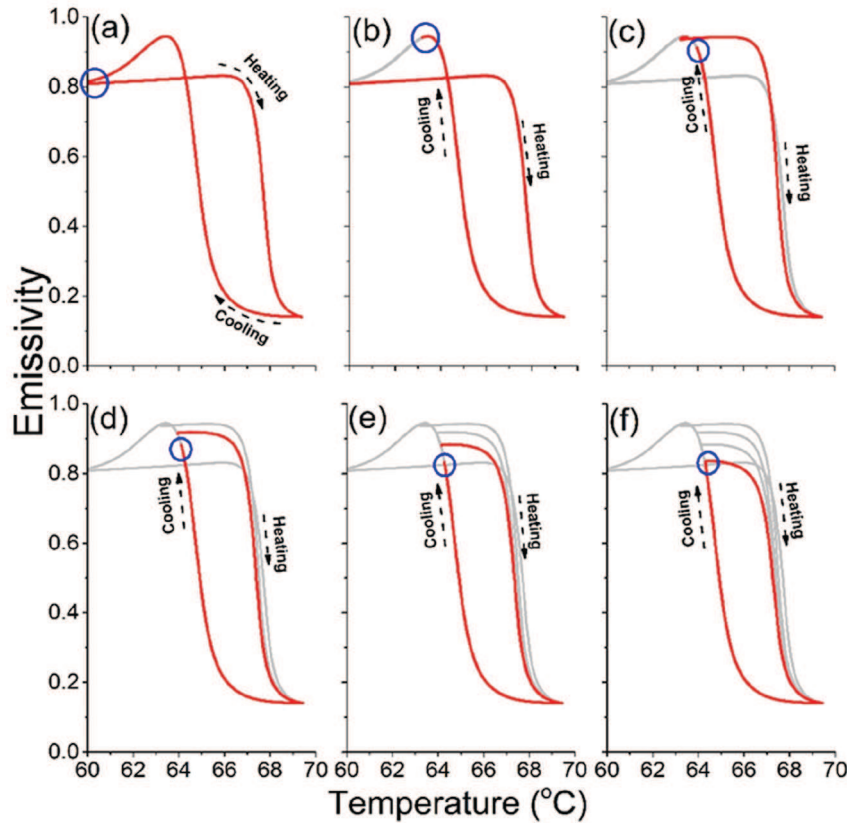


Fig. 5. Variable emissivity as shown from (a) to (f) is achieved by adjusting the minimal temperature of cooling cycle, and beginning the heating cycle immediately. Precise emissivity state can be reached by manipulating the cooling and heating temperatures.

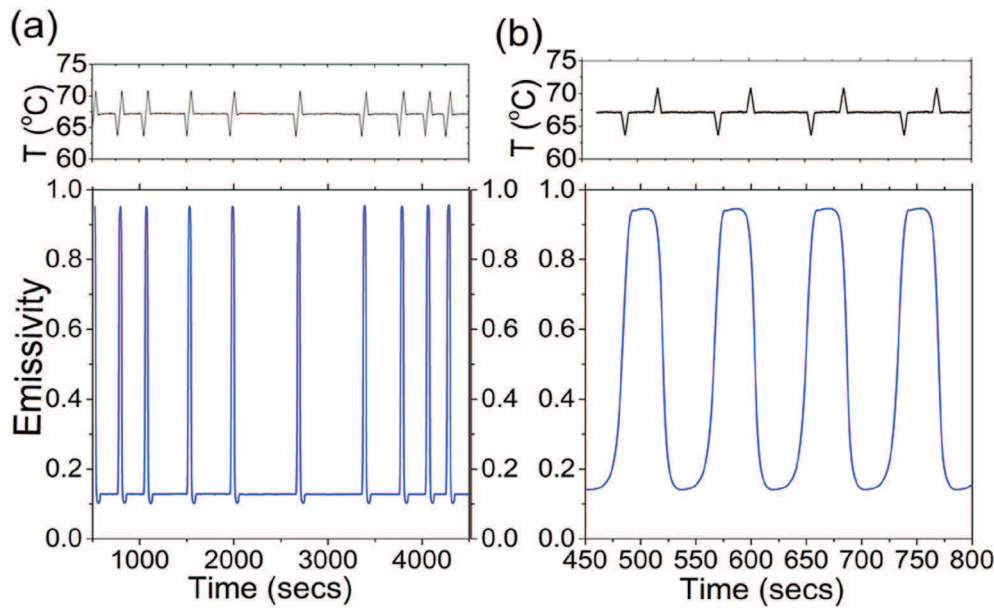


Fig. 6. Thermally-controlled emissivity switching with temperature pulses of $\pm 1.5^\circ\text{C}$ amplitude, operating as a (a) Blinker and (b) an On-off switch.

light modulation. High $\Delta\epsilon$ is achieved by providing small temperature pulses. These changes in emissivity are in fact a direct consequence of the variation in the topography of metallic inclusions in VO_2 metamaterial state. Hence a modular and tuneable emissivity state is reached by changing the size, shape and density of metal inclusions into a semiconducting matrix thus functioning as a smart cermet. We believe it is the first time VO_2 films are suggested to act as smart cermet.

In conclusion, smart cermet concept was introduced using VO_2 films in the metamaterial temperature range. VO_2 in particular and correlated oxides with SMT in general, can be ideal candidates for future light modulation, infrared reflectivity and thermal emissivity control to name a few. In this article, the optical modulation in VO_2 is thermally triggered. Electrical field [27] or mechanical stress [28] can also be implemented for the actuation of the SMT in VO_2 . Combining this strongly responsive material property with existing and upcoming technologies opens up countless possibilities to integrate innovative functionalities in light modulation and solar energy harvesting.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.mtphys.2017.12.002>.

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